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Synthesis and Photophysical Properties of Donor- and Acceptor-Substituted 1,7-Bis(arylalkynyl)perylene-3,4:9,10-bis(dicarboximide)s

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A series of 1,7-bis(arylethynyl)-*N,N′*-bis[2,6-diisopropylphenyl]perylene-3,4:9,10-bis(dicarboximide)s has been obtained from Sonogashira coupling of the 1,7-dibromoperylene-3,4:9,10-bis(dicarboximide) with *p*-substituted phenylacetylenes in which the *p*-substituents include π-donors (dialkylamino, diarylamino, *p*-(diarylamino)phenyl, alkoxy) and π-acceptors (diarylboryl, *p*-(diarylboryl)phenyl). The bis(arylethynyl)-substituted chromophores all show two reversible molecular reductions and are all slightly more readily reduced than unsubstituted perylene-3,4:9,10-bis(dicarboximide)s with the electrochemical potentials being rather insensitive to the π-donor or acceptor nature of the aryl group. The amine derivatives also show reversible molecular oxidations. The UV−vis spectra of the chromophores with alkoxy and boryl substituents show red-shifted absorptions relative to unsubstituted perylene diimides with discernible vibronic structure. In contrast, the lowest energy absorptions of the amino derivatives are broad and structureless, suggesting donor-to-acceptor charge-transfer character. Transient absorption spectra for the amine derivatives were interpreted in terms of ultrafast charge separation, followed by charge recombination on a time scale of ca. 80−2000 ps. Two compounds were also synthesized in which an additional stronger, but more weakly coupled, donor group is linked by a nonconjugated bridge to the *p*-amine donor, to investigate the effect on the charge recombination lifetimes; however, the lifetimes of the charge-separated states, ca. 150 and 1000 ps, were within the range observed for the simple amine systems. Finally, the two-photon absorption properties of three bis(arylethynyl)-substituted derivatives were investigated, along with those of 1,7-di(pyrrolidin-1-yl)-*N,N′*-bis[2,6-diisopropylphenyl]perylene-3,4:9,10-bis(dicarboximide). As with other perylene-3,4:9,10-bis(dicarboximide)s and related species, strong two-photon absorption (>1000 GM) was observed for three of these species close to the one-photon absorption edge; however, an additional feature (100−500 GM) was also observed at longer wavelength. An example with (*p*-aminophenyl)ethylnyl substituents showed a qualitatively different two-photon spectrum with a cross-section >500 GM being observed over a broad wavelength range.

Introduction

The properties of perylene-3,4:9,10-bis(dicarboximide)s (PDIs) (Figure 1), depending on their substitution pattern, can include highly exothermic electron affinities, high electron mobilities, and strong fluorescence. These properties have led to their use in fundamental studies of electron transfer and charge separation,[1−7] as subjects for single-molecule fluorescence studies,[8] as components of rotaxanes,[9,10] and as components of organic electron-transport materials with applications in devices including field-effect transistors and solar cells.[11−21] In addition, several PDI derivatives have been investigated as two-photon absorbing chromophores.[22−25]

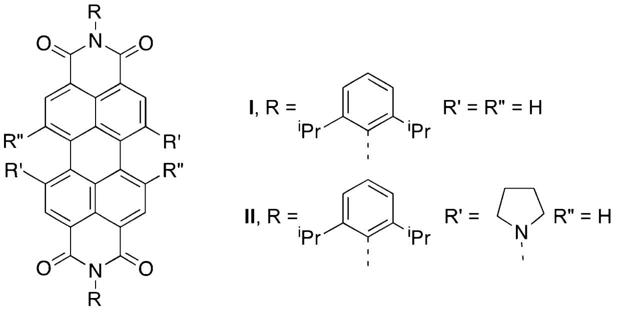

Figure 1. Generic structure of a PDI including two structures compared with the alkyne derivatives discussed in this paper.

Substitution at the 1, 6, 7, and/or 12 positions, typically via the intermediacy of halogenated PDI derivatives, offers the most flexible possibilities for modulating the electronic properties of this class of compound.[26] For example, 1,7-dicyano-substituted PDIs (Figure 1, R′ = CN, R″ = H) are significantly more easily reduced than the parent compounds.[27] 1,7-Diamino-substituted PDIs (such as **II**, Figure 1) show greatly red-shifted absorption bands,[28] which have been exploited in dye-sensitized solar cells.[29] π-Conjugated organic moieties can also be introduced

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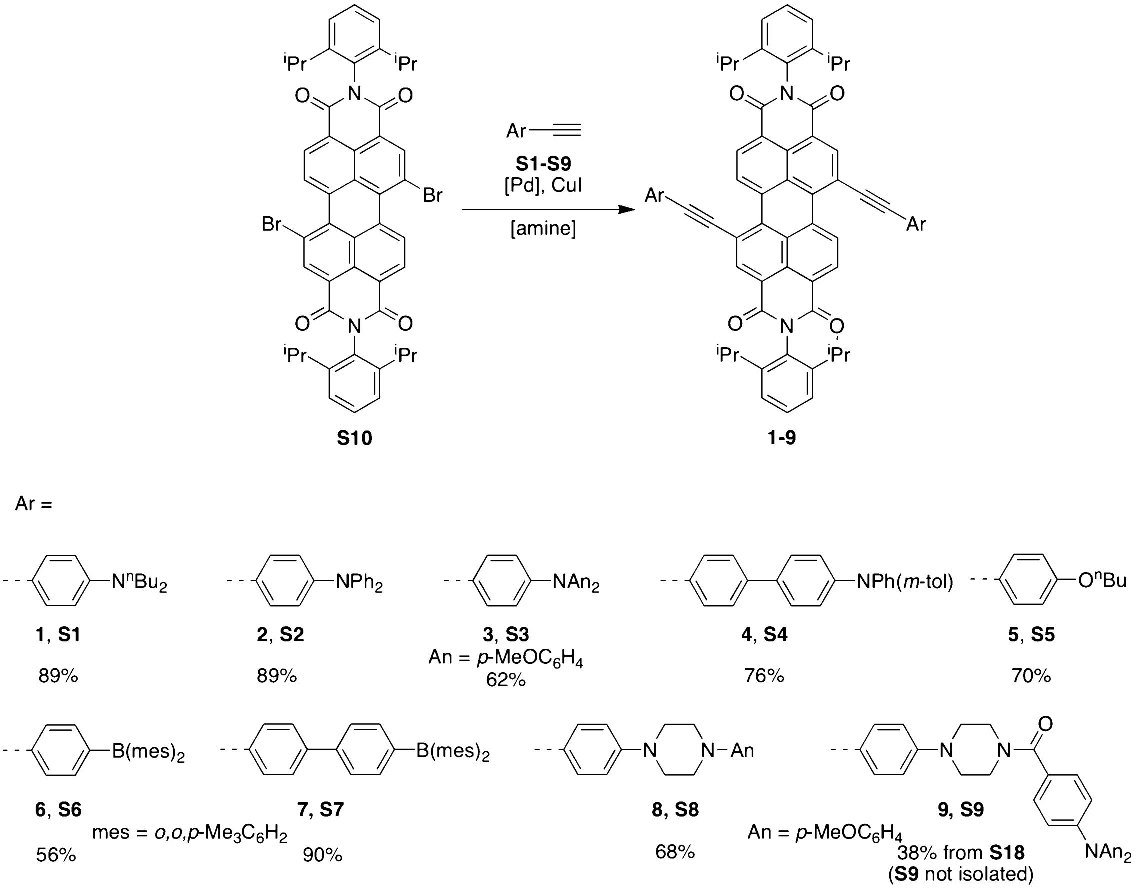
SCHEME 1: Syntheses and Yields for the 1,7-Bis(arylethynyl)-Substituted PDI Derivatives 1−9 Discussed in This Work from the Dibromo PDI S10 and the Relevant Arylethynes S1−S9, Respectively[a]



[a] Note: all PDIs were obtained as mixtures of two isomers in which the major 1,7 derivative (shown) is accompanied by the minor 1,6 isomer (not shown).

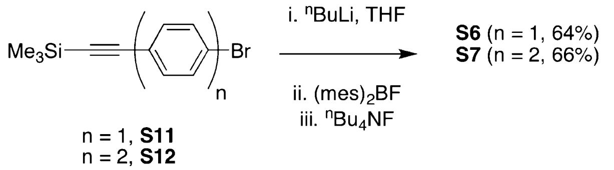
in these positions including aryl groups,[30−32] and oligothiophenyl[33,34] and dithienothiophenyl substituents.[35] In addition, phenylene groups have been used as bridges to other chromophores including other PDIs[36] and porphyrins,[7] and as points of attachment for nonconjugated bridges to coumarin and fluorol chromophores.[37] 1,7-Dialkynyl substituents have also been used, generally as intermediates in the syntheses of coronene diimide derivatives,[38−42] but also for electronically coupling phthalocyanines[43] to the PDI core.

Several systems in which porphyrin, phthalocyanine, and oligothiophene donors are linked to PDIs have been found to exhibit ultrafast intramolecular charge separation using transient absorption spectroscopy.[7,34,43] To investigate whether similar processes could be observed in systems containing simpler donors, such as amine derivatives, and to investigate the relevance of these processes to intermolecular charge separation, we have synthesized a series of 1,4-bis(arylethynyl)-*N,N′*-di[2,6-diisopropylphenyl]perylene-3,4:9,10-bis(dicarboximide)s (**1**−**7**, Scheme 1) in which the aryl groups are electron-rich relative to phenyl due the presence of amino or alkoxy groups (D) or are electron-poor due to diarylboryl susbtituents (A), leading to PDI derivatives with D−A−D (**1**−**5**) and A′−A−A′ (**6** and **7**) architectures. We have recently reported a time-resolved fluorescence and transient-absorption comparison of the 1,7-bis(4′-(diarylamino)biphenyl-4-ylethynyl) and 1,7-bis[(*p*-alkoxyphenyl)ethynyl] examples, **4** and **5**, respectively, in solid films.[44] While the observation of strong fluorescence quenching in films of **4** is consistent with the ultrafast *intra*molecular charge separation that we discuss in this work, transient absorption studies of films suggest a higher yield of *inter*molecularly charge-separated species in compound **5**. Here we report a solution study of the series of bis(arylethynyl) derivatives, **1**−**7** (Scheme 1), using electrochemistry and steady-state and transient absorption spectroscopy. In addition, compounds **8** and **9**, which incorporate additional amine groups that are not in conjugation with the core to afford D′···D−A−D···D′ structures (where "−" and "···" represent conjugated and nonconjugated bridging groups, respectively), are included in this study to further explore the possibility of increasing the lifetime of the charge-separated state. We have also investigated the two-photon absorption properties of D−A−D chromophores **1** and **5**, A′−A−A′ chromophore **6**, and an example of another type of D−A−D PDI: the previously reported 1,7-di(pyrrolidin-1-yl) derivative, **II** (Figure 1).[45]

Results and Discussion

Synthesis. The 1,7-bis(arylethynyl) PDIs **1**−**9** (Scheme 1) were prepared through Sonogashira[46] cross-coupling reactions of the appropriate terminal alkynes, **S1**−**S9**, respectively, with 1,7-dibromo-*N,N′*-di[2,6-diisopropylphenyl]perylene-3,4:9,10-bis(dicarboximide), **S10**,[47] using a variety of palladium catalyst systems. While $Pd(PPh_3)_4$ was an effective catalyst for the coupling reactions of the donor-substituted acetylenes (**S1**−**S5**), low yields (<20%) were observed in the coupling of the acceptor-substituted acetylenes (**S6** and **S7**). In the latter case, a $Pd(PhCN)_2Cl_2/P^tBu_3$ protocol[48] was found to give better reaction yields of ca. 60%. The D′···D−A−D···D′ compounds **8** and **9**, which were synthesized to investigate the effect of

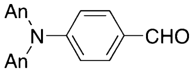
SCHEME 2: Syntheses of Triarylboron-Functionalized Alkynes



additional stronger, but more weakly coupled, donor groups on excited-state lifetimes (vide infra), were obtained using $Pd(PPh_3)_2Cl_2$ as the catalyst precursor.

The alkyne precursors were synthesized as described elsewhere (**S1**−**S5**),[44,49−51] or as shown in schemes 2−4 (**S6**−**S9**). The syntheses of **S7** and **S8** (Schemes 3 and 4, respectively) both employ additional palladium-catalyzed Sonogashira couplings. It should be noted that **S10** is obtained as a mixture of 1,6- and 1,7-dibrominated isomers, with the 1,6-isomer content varying in the range 5−30%. As a result, compounds **1**−**9** (and **II**) were also obtained as a mixture of isomers, which were generally not separable by silica gel chromatography. Accordingly, data are reported for the as-obtained mixtures and reference to that 1,7 isomer should be understood to mean the as-obtained mixture of 1,6 and 1,7 isomers.

Electrochemistry. Compounds **1**−**9** were studied using cyclic voltammetry in dichloromethane containing 0.1 M $[^nBu_4N][PF_6]$. Table 1 summarizes the potentials quoted relative to the ferrocenium/ferrocene couple. The PDI-based reductions for these species are compared to those for the parent PDI without substituents at the 1 or 7 positions, **I** (Figure 1),[52] and for another D−A−D derivative, the 1,7-di(pyrrolidin-1-yl) derivative, **II**.[45] Potentials for triarylamines **III**[53] and **S17** (Scheme 4) are also included for comparison with data for compound **9**. As expected, all the PDI derivatives undergo successive reversible reductions to the corresponding radical anions and dianions. The pyrrolidine-substituted compound, **II**, is 0.25 V less readily reduced than the unsubstituted PDI model compound, **I**, consistent with a previous report on a close analogue of **II** (in which the 2,6-diisopropylphenyl groups are replaced with cyclohexyl groups) in $^nPrCN/[^nBu_4N][ClO_4]$[28] and with the pyrrolidine substituents having a mild π-donor effect. In contrast, the (phenylalkynyl)-substituted PDIs, **1**−**9**, are all somewhat *more* readily reduced than **I**, regardless of whether the phenylalkynyl groups are substituted with π-donor or π-acceptor groups. There is little variation in the $E_{1/2}{}^{0/-}$ potentials with the variation in the aryl groups of **1**−**9**. These observations suggest that extension of conjugation is more important than the π-donor or acceptor groups in determining the LUMO energies of **1**−**9**. Indeed, DFT calculations for **4** and **5** reveal very similar LUMOs for the two molecules that are essentially composed of in-phase combinations of the local PDI LUMO with the local LUMOs of the ethynylene bridging groups.[44] The insensitivity of the $E_{1/2}{}^{0/-}$ potentials of 1,7-diaryl-substituted PDIs to aryl substituents has also previously been explained in terms of a PDI-localized LUMO.[30] The compounds with amine donors (**1**−**4**, **8,** and **9**) also exhibit reversible oxidations to the mono- and dications. In contrast to **II**, for which the two oxidations are separated by 0.14 V, no separation was observed between the two oxidations for **1**−**4**, **8,** and **9**.[54] In the case of the D′···D−A−D···D′ systems (**8** and **9**), additional reversible oxidations are also observed. The potentials corresponding to monocation and dication formation in these two species are less oxidizing than for **1**, suggesting that it is the secondary donors that are oxidized first and that the donors conjugated to the PDI core are only oxidized when the tri- and tetracations are formed. This interpretation is further supported by the observation that the first oxidation potential for **9** is close to that for acceptor-substituted triarylamine model compound **III**, and experimentally indistinguishable from that of **S17**.



III

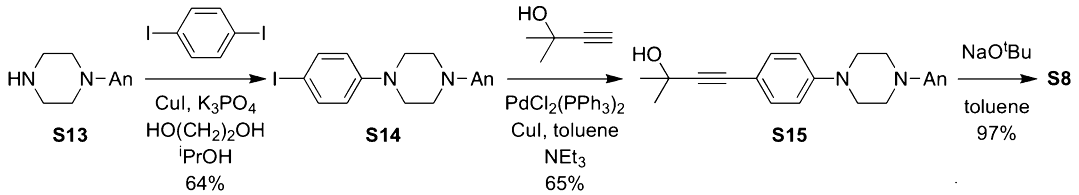
Steady-State Absorption Spectroscopy. The lowest energy feature in the spectra of unsubstituted PDIs such as **I** peaks at ca. 525 nm and has a well-defined vibronic structure.[55] In the bis(pyrrolidinyl)-substituted PDI, **II**, the donors destabilize the HOMO of the PDI core, leading to observation of a strong absorption with vibronic structure at considerably lower energy (with a weak structured band observed at higher energy).[1,28] Several of the 1,7-bis(arylethynyl) derivatives (**5**−**7**), i.e., those with π-accepting or weakly π-donating substituents, show spectra somewhat similar to that of **II** (Figure 2a); the lowest energy features of **5**−**7** all show maxima close to 600 nm, i.e., red-shifted relative to unsubstituted PDIs, but less strongly than that of **II**, and retain some resolvable vibronic structure, while another, weaker, feature is seen at ca. 450 nm. The similarity of the spectra of compounds **5**−**7** suggests, in agreement with the electrochemical data (see above), that extension of conjugation is the main effect in determining the electronic structure of these species.

The spectra of 1,7-bis(arylethynyl) derivatives **1**−**3**, in which the aryl group is a *p*-aminophenyl group (Figure 2b), are significantly different from those of **II** and **5**−**7**. In each case, the lowest energy feature (maxima between 664 and 718 nm) is an intense, structureless, relatively broad band, suggestive of a transition with considerable aminophenyl → PDI charge-transfer (CT) character, while a vibronically structured feature at higher energy (507−523 nm), in the vicinity of the absorption of the unsubstituted core, may be due to a PDI-centered transition. Further supporting a CT assignment, the energies of the low-energy absorption maxima (**1** < **3** < **2**) are those expected from the π-donor strengths of *p*-(dialkylamino)phenyl, *p*-[bis(*p*-alkoxyphenyl)amino]phenyl, and *p*-(diphenylamino)phenyl groups.[56]

The spectrum of **4** also shows a broad low-energy charge-transfer-type band, which is blue-shifted relative to those of **1**−**3** (Figure 2b), presumably due to the twisted biphenyl bridge between the donor and acceptor groups. The qualitative difference between **1**−**4** and **5**−**7** is supported by DFT and TD-DFT calculations on **4** and **5** that indicate the HOMOs to be primarily localized on the (diarylamino)biphenyl and PDI moieties, respectively.[44] The spectra of 1,7-bis[(*p*-aminophenyl)ethynyl] chromophores incorporating secondary donors (**8** and **9**) are similar to those of **1**−**3** (Figure 2c). Their low-energy absorptions are blue-shifted relative to that of **1**, consistent with previous computational investigations of the π-donor strengths of *p*-(di-*n*-propylamino)phenyl and *p*-(4-methylpiperazin-1-yl)phenyl groups.[56]

The differences between the spectra of **1**−**3** and those of **5**−**7** are reminiscent of those previously reported between the spectra of 1,7-bis[*p*-(diphenylamino)phenyl]-*N*,*N*′-di[2,6-diisopropylphenyl]perylene-3,4:9,10-bis(dicarboximide) and those of analogues in which the 1,7-diaryl substituents are varied from *p*-formylphenyl to *p*-methoxyphenyl.[30] The spectra for **1**−**3** also resemble those of 1,7-bis(oligothiophene)-substituted PDIs[33,34] and of dithieno[3,2-*b*:2,3-*d*]thiophene/PDI conjugated polymers[19,35,57]

SCHEME 3: Synthesis of (D′···D)-Substituted Alkyne S8



SCHEME 4: Synthesis of (D′···D)-Substituted Alkyne S9

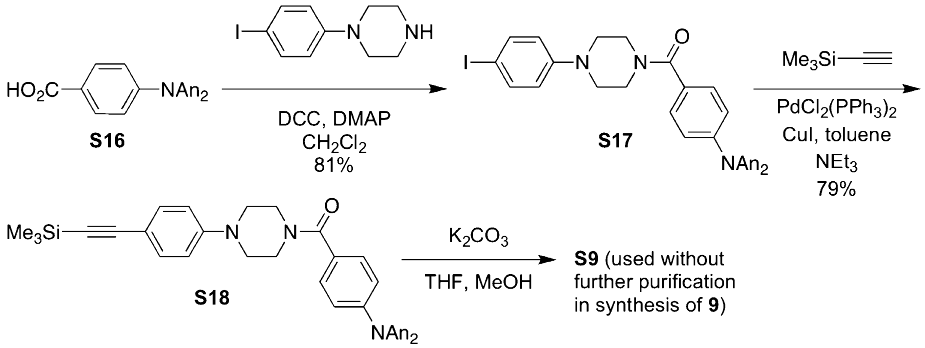
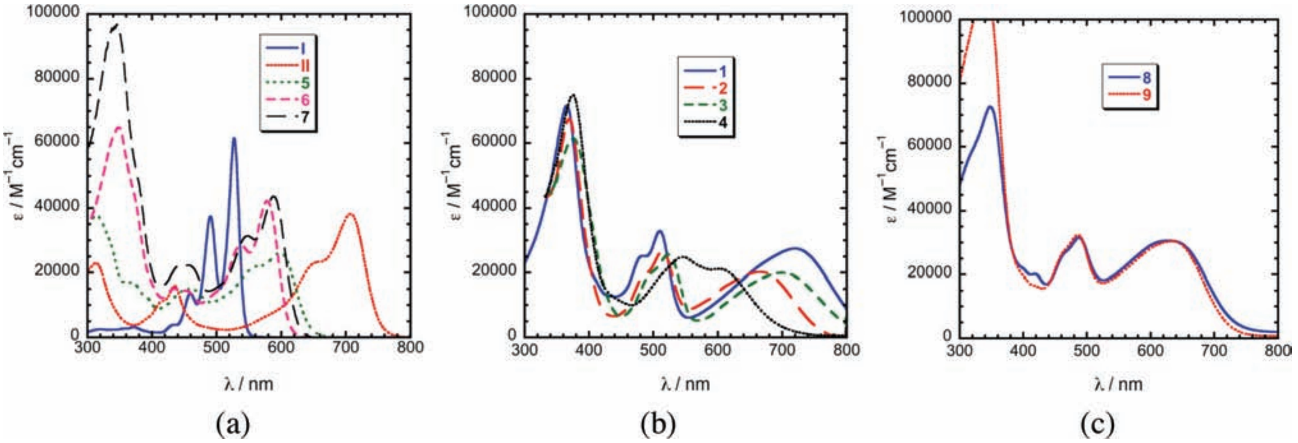


TABLE 1: Electrochemical Half-Wave Potentials (V) for PDIs 1−9 and Model Compounds I−III and S17 vs Ferrocenium/Ferrocene in Dichloromethane/0.1 M [^{n}Bu$_4$N][PF$_6$]

<table>
<tr><th></th><th>$E_{1/2}^{6+/5+}$</th><th>$E_{1/2}^{5+,4+}$</th><th>$E_{1/2}^{4+/3+}$</th><th>$E_{1/2}^{3+/2+}$</th><th>$E_{1/2}^{2+/+}$</th><th>$E_{1/2}^{+/0}$</th><th>$E_{1/2}^{0/-}$</th><th>$E_{1/2}^{-/2-}$</th></tr>
<tr><td>**1**</td><td></td><td></td><td></td><td></td><td colspan="2">+0.48[a]</td><td>−0.97</td><td>−1.15</td></tr>
<tr><td>**2**</td><td></td><td></td><td></td><td></td><td colspan="2">+0.61[a]</td><td>−0.92</td><td>−1.21</td></tr>
<tr><td>**3**</td><td></td><td></td><td></td><td></td><td colspan="2">+0.29[a]</td><td>−0.95</td><td>−1.14</td></tr>
<tr><td>**4**</td><td></td><td></td><td></td><td></td><td colspan="2">+0.49[a]</td><td>−0.90</td><td>−1.09</td></tr>
<tr><td>**5**</td><td></td><td></td><td></td><td></td><td></td><td></td><td>−0.93</td><td>−1.12</td></tr>
<tr><td>**6**</td><td></td><td></td><td></td><td></td><td></td><td></td><td>−0.89</td><td>−1.09</td></tr>
<tr><td>**7**</td><td></td><td></td><td></td><td></td><td></td><td></td><td>−0.89</td><td>−1.09</td></tr>
<tr><td>**8**</td><td></td><td></td><td colspan="2">+0.77[a,b]</td><td colspan="2">+0.28[a]</td><td>−0.95</td><td>−1.13</td></tr>
<tr><td>**9**</td><td colspan="2">+0.98[a]</td><td colspan="2">+0.62[a]</td><td colspan="2">+0.31[a]</td><td>−0.94</td><td>−1.13</td></tr>
<tr><td>**I**</td><td></td><td></td><td></td><td></td><td></td><td></td><td>−1.01</td><td>−1.23</td></tr>
<tr><td>**II**</td><td></td><td></td><td></td><td></td><td>+0.38</td><td>+0.24</td><td>−1.27</td><td>−1.41</td></tr>
<tr><td>**III**</td><td></td><td></td><td></td><td></td><td></td><td>+0.42</td><td></td><td></td></tr>
<tr><td>**S17**</td><td></td><td></td><td></td><td></td><td>+0.64</td><td>+0.31</td><td></td><td></td></tr>
</table>

[a] The integrated areas of these features were ca. twice that of the features assigned to each one-electron PDI-based molecular reduction, suggesting that these features correspond to two overlapping molecular oxidations occurring at similar potentials. [b] EC-type process.



(a) (b) (c)

Figure 2. UV−visible absorption spectra of **I**, **II**, and **1**−**9** in toluene: (a) derivatives in which the low-energy bands of the spectra retain some vibronic structure; (b) bis[(aminophenyl)ethynyl] D−A−D derivatives having low-energy charge-transfer-type bands; and (c) D′···D−A−D···D′ systems.

and small-molecule model compounds.[35] Moreover, a quantum-chemical study of the 1,7-diaryl species indicated qualitative differences in the HOMOs of the species with amino donors from those with weaker π-donors or π-acceptors,[30] similar to the differences evident in the HOMOs of **4** and **5**.[44]

Radical-Ion Spectra. To the best of our knowledge, electronic spectra have not hitherto been reported for PDI radical anions bearing extended conjugation in the 1,7 positions. To address this deficiency and to assist in the interpretation of transient spectra (vide infra), the radical anions of **1**−**9** have

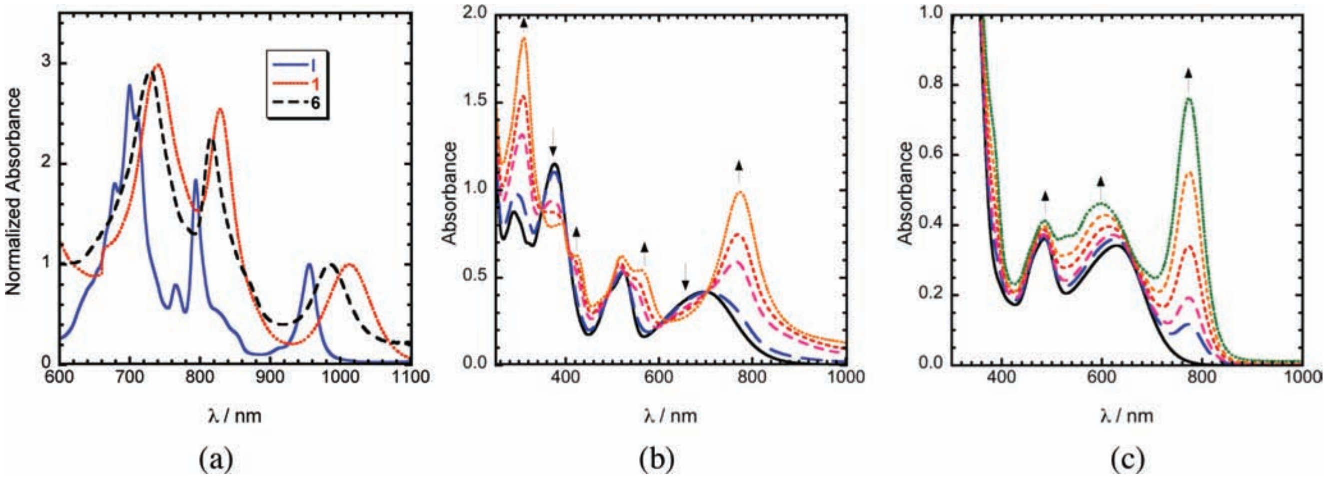


Figure 3. Spectra of radical ions of bis(arylethynyl)-substituted PDIs: (a) radical anions of **1** and **6**, with that of **I** for comparison, generated by reduction with cobaltocene in THF; (b) and (c), sequential oxidations of **3** and **9**, respectively, with tris(*p*-bromophenyl)aminium hexachloroantimonate in dichloromethane.

been generated in THF solution by reduction with cobaltocene ($E_{1/2}{}^{+/0} = -1.33$ V in CH$_2$Cl$_2$[58]). Figure 3a compares the spectra of $\mathbf{1}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ to that of $\mathbf{I}^{\bullet-}$, which is typical of the spectra of unsubstituted PDI radical anions.[59,60] The spectra of the 1,7-bis(arylphenylethynyl) species are similar to one another; in particular, spectra for $\mathbf{5}^{\bullet-}$, $\mathbf{6}^{\bullet-}$, and $\mathbf{7}^{\bullet-}$ are nearly identical, while the amine-substituted spectra are red-shifted relative to these species to varying degrees, with that of $\mathbf{1}^{\bullet-}$ being the most red-shifted (data for all nine species are given in the Supporting Information). Although, the spectra are red-shifted and broadened relative to those of $\mathbf{1}^{\bullet-}$, they are similar to those of a 1,6,7,12-tetrakis(aryloxy) PDI anion,[10] and the presence of three distinct low-energy peaks at wavelengths between 700 and 1100 nm strongly suggests that the excess electrons of the molecular anions are largely localized on the PDI portion of the molecule. Spectra of $\mathbf{3}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ (Figure 3b,c) were also obtained in dichloromethane after oxidation with tris(*p*-bromophenyl)aminium hexachloroantimonate ($E_{1/2}{}^{+/0} = +0.70$ V in CH$_2$Cl$_2$[58]). In both cases, oxidation leads to a new peak at ca. 775 nm, which may be due to formation of a triarylaminium radical cation (simple triarylaminium ions absorb in the range ca. 630−830 nm and the oxidant absorbs at 710 nm[61]). Oxidation of **3** is accompanied by the disappearance of the low-energy charge-transfer-type band of the neutral compound, whereas in **9** this band is only moderately blue-shifted and actually increases slightly in intensity, suggesting that the D−A−D core remains intact (the blue shift in the bands perhaps reflecting a reduction in the donor strength of the primary donor through electrostatic interactions with the oxidized triarylamine), i.e., that oxidation occurs at the triarylamine D′ group.

Transient Absorption Spectroscopy. A wide variety of architectures composed of donors and PDI acceptors have been found to undergo photoinduced charge separation;[7,34,43,62] however, in only a few of these systems are the donor and PDI potentially in π-conjugation,[7,34,43,63] and in even fewer are donor and acceptor sufficiently strongly coupled that the electronic spectra show similar CT-type absorptions to **1**−**4**, **8**, and **9**.[34,35] Therefore, the current systems provide an opportunity to more fully understand photoinduced electron transfer in strongly coupled donor−PDI systems. We investigated this possibility for compounds **1**−**6**, **8**, and **9** using transient absorption spectroscopy in toluene with 400 nm as the excitation wavelength. For **8** and **9** we also acquired data with 620 nm excitation (i.e., exciting into the low-energy CT-type absorption) and found results similar to those obtained by excitation at 400 nm. Transient spectra for **1**, **4**, **5**, and **8** are shown in Figure 4 with the remaining examples shown in the Supporting Information. The temporal evolution of the spectra was in each case fitted with two time constants, τ_R and τ_D; these values are summarized in Table 2. In all cases, a bleaching of the neutral ground-state absorption features is evident and the initially formed excited state rapidly evolves on the picosecond time scale (τ_R being in the range ca. 5−10 ps) to give species with lifetimes (τ_D) ranging from ca. 80 ps to ca. 3 ns. In the case of the bis[*p*-(dimesitylboronyl)phenylethynyl] A′−A−A′ chromophore, **6**, for which one would not expect charge separation, the relatively long-lived state has a rather featureless broad absorption in the near-IR with no well-defined peak maximum in the wavelength range investigated (see Supporting Information). The bis[(*p*-alkoxyphenyl)ethynyl] derivative, **5** (the steady-state absorption spectrum of which is similar to that of **6**, vide supra), shows transient spectra (Figure 4c) similar to those for **6** (see Supporting Information) and a very similar τ_D.

In the case of the species with amino donors, **1**−**4**, **8**, and **9**, τ_D are all shorter than those for **5** and **6**, although varying considerably (over more than an order of magnitude) from compound to compound. For some examples, one or more well-defined maxima are observed in the 700−775 nm range. Since the radical anions and cations of these compounds (vide supra) absorb in this wavelength range, these maxima most likely indicate the formation of a charge-separated state. For example, the maxima seen in the transient spectra of **4** (Figure 4b) at ca. 700 and 750 nm are close in wavelength to both features in the spectra of $\mathbf{4}^{\bullet-}$ and to the absorption maximum expected for a triarylaminium radical cation. The qualitative difference in transient spectra between the amino derivatives and compound **5** and **6** parallels the differences noted above in absorption spectra, and also the differences in HOMOs between **4** and **5**, that of **4** being much more strongly localized on the donor group.[44]

The range of decay time constants, τ_D, found for **1**−**4**, **8**, and **9** fall in the same range as those seen for photoinduced CT states in other strongly coupled donor−acceptor PDIs. For example, photoexcitation of a 1,7-dialkynyl substituted PDI with zinc phthalocyanine donors in place of the aminoaryl donors of the present study gives a charge-separated state characterized by a lifetime of 517 ps in toluene.[43,64] For PDIs with oligothiophenyl and dithiothiophenyl substituents, charge-separation

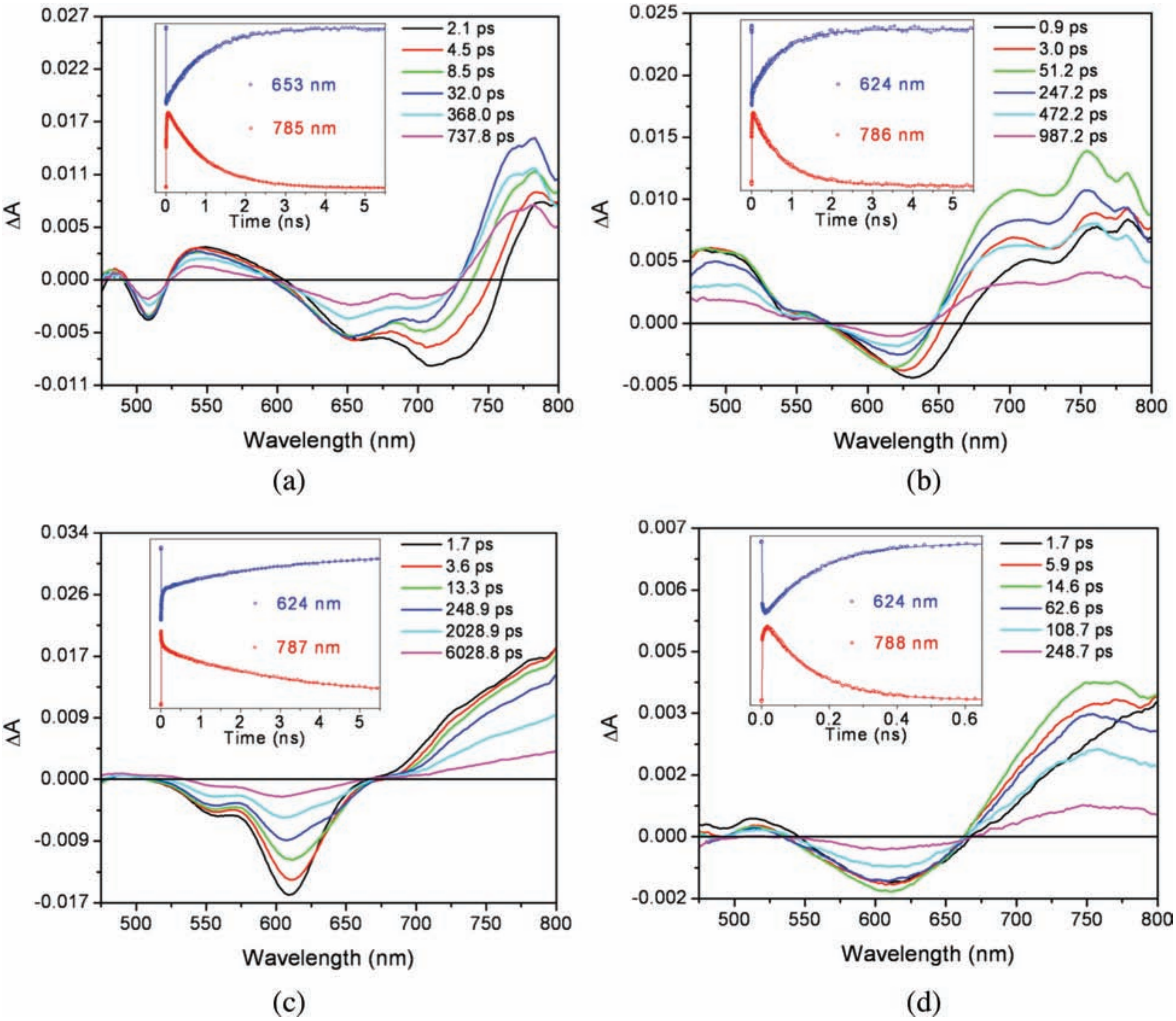


Figure 4. Transient absorption of compound **1** (a), **4** (b), **5** (c), and **8** (d) in toluene after excitation at 400 nm (left) and after decay of the excited states at various wavelengths (right).

TABLE 2: Lifetimes Characterizing the Transient Absorption Behavior of PDI Derivatives after Excitation (at λ_{ex}) in Toluene[a]

compound	λ_{ex}/nm	τ_R/ps	τ_D/ps	$-\Delta G_{CS}{}^a$/eV	$-\Delta G_{CR}{}^a$/eV
1	400	6.0 ± 0.2	960 ± 20	0.51	1.49
2	400	13.4 ± 1.1	2090 ± 70	0.39	1.62
3	400	4.7 ± 0.7	82 ± 2	0.49	1.51
4	400	10.5 ± 0.6	770 ± 30	0.24	1.76
5	400	7.0 ± 0.3	3070 ± 170		
6	400	5.4 ± 0.6	3220 ± 170		
8	400	7.7 ± 1.0	141 ± 6	0.32	1.68
	620	7.9 ± 0.8	151 ± 2		
9	400	6.8 ± 0.3	829 ± 7	0.30	1.70
	620	9.0 ± 0.6	1003 ± 6		

[a] Estimated as described in the text.

and recombination time scales were in the range 0.33−7.9 and 21−1462 ps, respectively, depending on the specific structures and the solvent (CH_2Cl_2 or $CHCl_3$).[34,35] While many systems without conjugation between donor and acceptor also show charge-separated-state lifetimes in the same range, much longer lived charge-separated states have been obtained in some examples; for example, a lifetime of 240 μs has been obtained in a zinc phthalocyanine/PDI dyad with a nonconjugated linker in the presence of Mg^{2+};[65] however, in many cases these more weakly coupled systems also show less rapid charge separation. Although the rates of charge separation and recombination, k_{CS} and k_{CR}, respectively, in many weakly coupled donor−acceptor systems, including some of these PDI systems, can be correlated with the estimates of the free-energy changes for these processes, ΔG_{CS} and ΔG_{CR}, respectively, obtained from electrochemical and optical data,[2,7,66,67] the presence of strong CT-type absorption bands in **1**−**4**, **8**, and **9** indicates that the amine donors in these molecules are strongly coupled to the PDI acceptors, rendering the Weller formalism[67] for estimating ΔG_{CS} and ΔG_{CR} inappropriate. Hence, we estimated ΔG_{CS} as the difference between the energy of the PDI-localized state, as given by the low-energy onset of the absorption band of **6** (2.00 eV), and that of the charge-separated state, estimated by the onsets of the absorption bands for **1**−**4**, **8**, and **9**.[68] Similarly, the low-energy onset of the CT-type absorption bands of **1**−**4**, **8**, and **9** were used to estimate the corresponding values of ΔG_{CR}. The finite rise times (τ_R) observed in the transient spectra (Figure 4) most likely represent relaxation from the vertically excited PDI-based state to a CT state. The values of k_{CS} ($=1/\tau_R$) are more-or-less independent of ΔG_{CS} over this relatively small range of free energies, which is not surprising given that the absorption spectra (and, for **4**, TD-DFT calculations[44]) suggest that the vertical excited state already has considerable CT character and, therefore, that formation of the CT state may be an adiabatic process. The decay rate constants of the **1**−**4**, **8** and **9** CT states, k_{CR} ($=1/\tau_D$), also show no clear dependence on ΔG_{CR}, which again can be explained in terms of the adiabatic nature of the charge recombination within these molecules.

Compounds **8** and **9** were synthesized with the aim of promoting a secondary, thermal charge separation to obtain species of the type $D'^{\bullet+}\cdots D{-}A^{\bullet-}{-}D\cdots D'$, which might be expected to extend the lifetime of the charge-separated state. Surprisingly, the value of τ_D for **8** is significantly *shorter* than that of the simpler D−A−D structural analogue, **1**, in spite of the fact that the CT state energy is somewhat higher than that of **1**, while the value of τ_D for **9** is similar to that of **1**. A possible explanation for the lack of correlation of the CT lifetimes with **8** and **9** with the energies is that the CT lifetimes are influenced largely by electronic coupling between the secondary donor and the CT state. The piperazine nitrogen atom that is bonded to the *p*-MeO−phenyl group in **8** is perhaps implicated in this coupling since reducing the ability of the lone pair of electrons on that nitrogen atom to interact with the CT state by converting it to an amide in **9** lengthens the CT state lifetime.[69] In any case, it is clear that the strong electronic coupling between the primary donors and acceptors in this series of molecules makes it difficult to dissect the interactions between them in the straightforward way that is usually possible for nonadiabatic electron transfers.

Two-Photon Absorption Spectra. Several studies have examined the two-photon absorption (2PA) properties of PDIs and related chromophores.[22−25] However, while 2PA cross sections at a single wavelength (850 nm) have been measured for some 1,2,6,7-tetraalkoxy-substituted PDI derivatives,[24] no 2PA *spectra* have previously been reported for PDI derivatives with substituents in the 1,7 positions. In particular, the success achieved in obtaining large 2PA cross sections in phenylenevinylene-based molecules and related systems using quadrupolar D−A−D structural motifs,[70] suggests that D−A−D species, such as **I**, may be interesting candidate 2PA chromophores. The 2PA spectra of four of the present PDI derivatives were investigated; **1** and **II** were studied using the open-aperture Z-scan technique[71] while **5** and **6** were studied using two-photon-induced fluorescence.[72] The 2PA spectra are shown in Figure 5 plotted as function of photon wavelength (spectra plotted as a function of transition energy are provided in the Supporting Information). As in previous studies of PDIs and related chromophores[22−25] the spectra of **I**, **5**, and **6** are dominated by the onset of a strong absorption as the photon energy approaches that of the low-energy one-photon transition, i.e., at small detuning energies. Thus a 2PA-active state presumably lies close to twice the energy of the 1PA state in these compounds; the small detuning energy between the two-photon energy and the energy of the 1PA state is likely to be an important contributory factor to the large 2PA cross sections. Other chromophore classes found to exhibit large 2PA cross sections at small detuning energies include squaraines,[73,74] porphyrin oligomers,[75,76] and nickel dithiolene complexes.[77] In the case of **1**, an onset was less clearly defined; however, in this compound it was not possible to measure 2PA cross sections as close to the 1PA peak due to **1** exhibiting a much broader low-energy tail to its lowest energy 1PA feature. Additional two-photon absorption features at lower energies (longer wavelengths) are considerably weaker than the near-double-resonance feature close to the 1PA edge. While a detailed interpretation of these features is beyond the scope of the present work, a few trends can be noted. In the well-resolved spectra of both **5** and **6**, shoulders with cross sections of ca. 200 GM are discernible at ca. 800 nm and correspond to excitation into a state at ca. 1.5 times that of the 1PA state energy (the spectra are replotted vs state energy in Figure S3 to facilitate comparison); a similar, but stronger (ca. 1000 GM), feature is seen at ca. 1.5 times the energy of the 1PA state for a simple PDI.[23] At lower energy still, the 2PA spectra of **5**, **6**, and **II** display a two-photon peak corresponding to excitation at ca. 1.25 times the 1PA state energy, while no features are seen in this energy range for a simple PDI.[23] In the case of **1**, the low-energy part of the 2PA spectrum is broad, with a cross-section of ca. 500 GM extending over a wide wavelength range, perhaps indicating the presence of several 2PA states close in energy and perhaps partly due to 2PA bands comparably broad to the low-energy 1PA absorption. However, in all four compounds the peak cross sections seen for the low-energy features are smaller than those that have been reported for D−A−D phenylenevinylene-based chromophores that have comparable or smaller numbers of π electrons.[78,79]

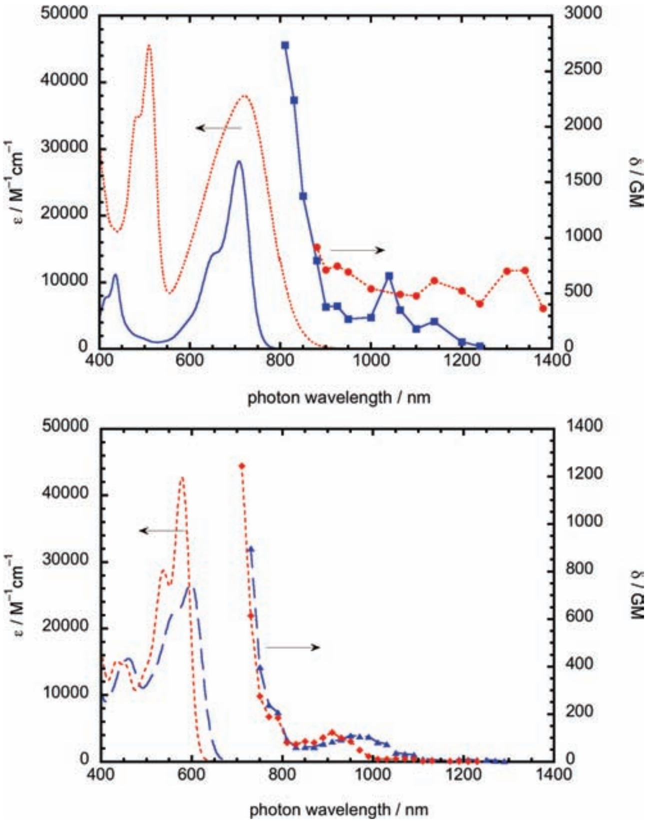


Figure 5. Top: one-photon (lines) and two-photon (lines with data points) spectra of **II** (blue, solid line, squares), **1** (red, dotted line, circles). Bottom: one-photon (lines) and two-photon (lines with data points) spectra of **5** (blue, long dashes, triangles), and **6** (red, short dashes, diamonds) in dichloromethane. The spectra are also shown replotted as a function of transition (state) energy in the Supporting Information.

Conclusions

A series of 1,7-bis(arylethynyl) PDIs has been synthesized. Extension of conjugation slightly increases the ease of reduction of these species, with the π-donor or -acceptor nature of the aryl group having only minor effects. The UV−vis absorption spectra, on the other hand, are strongly dependent on the nature of the substituent. Whereas the low-energy absorptions of examples with aryl = *p*-alkoxyphenyl (**5**), *p*-(diarylboryl)phenyl (**6**), and 4′-(diarylboryl)biphenyl-4-yl (**7**) substituents are vibronically structured and occur at similar energy to one another, those of the aryl = *p*-aminophenyl (**1**−**3**, **8**−**9**) and 4′-aminobiphenyl-4-yl (**4**) derivatives generally occur at lower energy and do not exhibit vibronic structure. These differences are in line with previous observations for 1,7-diaryl-substituted PDIs,[30] and with qualitatively different orbital structures for amino-substituted species, as previously demonstrated computationally for **4** and **5**.[44] Transient absorption measurements also indicate similarities between **5** and **6**, both ultimately forming excited states with lifetimes of ca. 3 ns, while the behavior of **1**−**4**, **8**, and **9** suggests ultrafast CT state formation, followed by charge recombination on time scales of 2 ns or less. The low-energy CT-type bands seen in the absorption spectra of these species allows for the creation of charge-separated states using longer wavelength light than is possible for many other PDI donor−acceptor systems. However, attempts to lengthen the lifetime of the charge-separated state by adding a secondary donor in **8** and **9** were unsuccessful, with **8** even showing a markedly *shorter* charge recombination lifetime than the other chromophores. Development of systems showing improved lifetimes will require careful control of the electronic coupling between primary and secondary donors, D and D′, respectively, to achieve secondary charge separation that is competitive with charge recombination, while at the same time minimizing back electron transfer. An additional possibility may be that the electrostatic attraction between hole and electron in the initially formed $D' \cdots D^{\bullet +}-A^{\bullet -}-D \cdots D'$ charge-separated state makes the secondary charge transfer unfavorable in **8** and **9**,[69] outweighing the small difference in redox potentials between the D and D′ sites, in which case future work should also employ stronger secondary donors. Two-photon absorption spectra for **5** and **6**, along with a 1,7-di(pyrrolidin-1-yl) PDI (**II**) indicate that these compounds are similar to unsubstituted PDIs in exhibiting large two-photon absorption cross sections close to their one-photon absorption edges; as with the one-photon peaks, these two-photon features are red-shifted relative to their unsubstituted analogues. However, additional, relatively weak, lower energy 2PA features not observed in an unsubstituted PDI[23] are observed in the near-IR. Compound **1**, a representative of the (*p*-aminophenyl)ethynyl PDIs **1**, which, exhibit qualitatively different 1PA spectra from the other chromophores, also has a qualitatively different 2PA spectrum in which the high-energy onset of strong 2PA is less clearly defined and in which the lower energy features extend over a wide wavelength range.

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Supporting Information Available: Spectra of the radical anions of **1**−**9**; transient absorption spectra for **2**, **4**, **6**, and **9**; alternative presentations of the 2PA spectra for **II**, **1**, **5**, and **6**; experimental details for the photophysical measurements; and synthetic details and characterization for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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